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PREPARATION AND CHARACTERIZATION OF HYDROXYAPATITE – ZIRCONIA COMPOSITE

Thesis submitted in partial fulfillment as a requirement for the degree of Bachelor of Technology under the guidance of Professor SUDIP DASGUPTA

By

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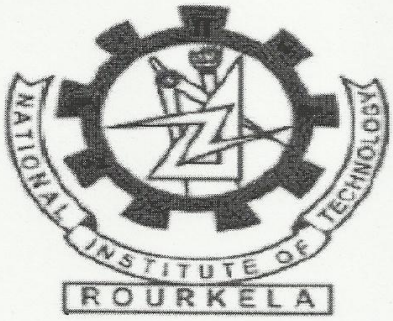
2012- 2013



CERTIFICATE

This is to certify that the project entitled "**Preparation and characterization of hydroxyl apatite-zirconia composite**" submitted by Sudip Sukla Baidya is a genuine work performed by him under my guidance required for the **Bachelor of Technology degree** in **Ceramic Engineering** at **National Institute of Technology**, Rourkela

To the best of my knowledge, this thesis is very authentic and none of its matter has been submitted anywhere else for the award of degree or diploma.

Sudip Dasgupta
13.05.13

Professor Sudip Dasgupta

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ACKNOWLEDGEMENT

I would like to thank my guide and mentor Professor Sudip Das Gupta with all my heart. He has been very helpful and was always ready whenever I faced troubles regarding the project. He had given some excellent ideas and without his guidance this work would have been incomplete.

I would also like to thank the faculty and staff who were always in the department and their small little suggestions really helped a lot.

Also thanks to all the PhD scholars and M.Tech students who were always ready with their helpful hands and made this project a successful one. Special thanks to Mr. Kanchan Maghi, a PhD scholar who has been the most helpful one.

And lastly thanks to all my friends who backed me up with their moral support and always motivated me throughout the project.

SUDIP SUKLA BAIDYA

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ABSTRACT

In this present study, sintered hydroxylapatite-zirconia composites were processed and characterized. Hydroxylapatite and both undoped and doped zirconia powders were synthesized using precipitation method. To synthesize partially stabilized zirconia (PSZ) and tetragonal stabilized zirconia (TZP) 2.5 mol% and 7.5 mol% of Ca^{2+} were added to precursor material for zirconia synthesis. Though HA powders showed the presence phase pure hydroxyapatite a mixture of monoclinic and tetragonal zirconia phases were observed in undoped zirconia, PSZ and TZP powders. Zirconia was added to the extent of 5, 10 and 15 wt% to HA powder and consolidated into pellets and sintered at 1250^{o}C to prepare HA-ZA, HA-PSZ and HA-TZP composite. XRD study of sintered composites showed the presence of tricalcium phosphate (TCP) as a result of decomposition of HA at 1250°C in presence of zirconia. HA-5 wt% ZA composition showed the highest bulk density, Vickers hardness and bi axial flexural strength. This study shows that mechanical strength of HA can be improved after addition of both stabilized and unstabilized zirconia and HA-ZrO_2 based composite orthopedic implant can be used in moderately load bearing applications where sole hydroxyapatite implant may fail.

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CHAPTER # 1

INTRODUCTION

Bioceramics are an important subset of biomaterials. The term bioceramics are being used for those manmade materials which are being used as medical implant and exhibit specific positive response within the body aimed for the repair or augmentation of damaged tissue and/or skeletal parts. Bioceramics range in biocompatibility from the ceramic oxides, which are inert in the body, to the other extreme of resorbable materials, which are eventually replaced by the materials which they were used to repair. Bioceramics are used in many types of medical procedures. Dental and bone implants are the common applications of bioceramics.

Improvement in modern health care has significantly enhanced the life expectancy and quality of human life. With the advancement of civilization the need for advanced biomaterials to treat bone defects and repairs is growing, particulary for aging population. Although significant research has been done, developing new materials to mimic both functions and structures of natural tissues is still a far way to go. Over the past few decades, interest in bioceramics has increased to such a point that today they are used not only in making eyeglasses, tissue culture flasks, and thermometers, but ceramics materials are increasingly being used for the repair and reconstruction of skeletal diseases and disorders.[1-4]

Apatite related calcium phosphate (CaP) minerals have crystallographic and chemical characteristics similar to various hard tissues such as bones and teeth of vertebrata. Among various CaPs, hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] is the most widely used ceramic for bone tissue repair and reconstruction. Synthetic HA shows excellent biocompatibility with hard tissues, skin, and muscle tissues. Although HA-coated implants are often used as load-bearing implants, the medical applications of pure HA ceramics are limited to non load bearing areas such as powders, coatings, and porous scaffolds due to their low strength and fracture toughness.[5] In order to improve mechanical reliability of HA ceramics, it is important to improve both strength and toughness of HA structures.

Zirconia (ZrO_2) based ceramics have been gaining much attention in recent years [6, 7] because of their relatively high fracture toughness compared with other ceramics. ZrO_2 is a relatively bio-inert material and as such, ZrO_2 and ZrO_2 toughened ceramics have been used as components in femoral head replacement prostheses [8, 9] and as dental restorative materials due to suitable aesthetics and wear resistance[10]. Several ceramic materials benefit from the addition of ZrO_2 inclusions to improve their hardness/toughness and wear characteristics, including alumina (ZrO_2 toughened alumina, ZTA) and mullite (ZrO_2 toughened mullite, ZTM)[10, 11].

Hydroxyapatite -zirconia composites have received much attention during the last decade due to their combination of the desirable mechanical properties of zirconia and the excellent bioactivity of hydroxyapatite (HA). However, thermal decomposition of the hydroxylapatite phase and reaction between the zirconia phase and the hydroxyapatite phase remain a major problem of the hydroxyapatite-zirconia composites. However the strength can be increased using oxide reinforcements such as zirconia. High sintered density and ultra fine particles (in the nano range) along with the use of stabilizers will ensure ZrO_2 mostly in tetragonal phase leading to improved mechanical properties of the composites. This present work is being carried out to see how zirconia affects the strength of the HA and the use of the composite in biomedical applications.

CHAPTER # 2

LITERATURE SURVEY

Because of its chemical composition and crystallographic structure similar to those of human hard tissues, hydroxyapatite (HA) has been extensively studied for use as bone and tooth implants . However, as HA is intrinsically poor in mechanical properties, bone replacement parts made from HA have been used only in non-load-bearing areas such as the ossicles in the middle ear. Therefore, for full utilization of bioactive HA-based implants, improvements in mechanical properties are necessary. Ceramics materials in form of oxides are the most commonly used and also found in great quantities in nature. The chemical synthesis, shaping and heat treatment processes of oxides are relatively simple compared to other materials. The properties common to all ceramics are chemical stability, low density, high hardness, low tensile strength and high compressive strength. Ceramics are ideal materials for mobile load bearing components in aggressive environments such as engine blocks, refractories and hard tissue replacements. Body is an active system regularly maintaining itself with its defense mechanism for optimum working conditions. A continuous process of building up and breaking down of biostructures provides a demanding aggressive environment for body components. The actions of living cells as a part of the immune system are on the nanoscale and are basically chemical dissolution and adsorption processes. Following contact with body tissue, bare surface of a biomaterial is covered rapidly with proteins that are adsorbed from the surrounding body fluids. The chemistry of the underlying substrate, due to its effect on wettability and surface charge, controls the nature of the adherent protein layer. Macrophage fusion and platelet adhesion are strongly dependent on surface chemistry. Although cells are able to adhere, spread and grow on bare biomaterial surfaces in vitro, proteins adsorbed from the adjacent tissue environment and adherent cells enhance cell attachment, migration and growth. Cell adhesion to biomaterials is mediated by cytoskeletal associated receptors in the cell membrane which interact with cell adhesion proteins that adsorb to the material surface from the surrounding plasma. The chemical nature of a biomaterial placed in the body as an implant therefore is important in functioning of the body. Some ceramics

that have been tested in vivo do not cause increased activity of immune system when dissolved in body fluid or in contact with tissues. Such ceramics, mainly oxides, are termed bioceramics. Bioceramics have the advantage of being compatible with the human body environment. Their biocompatibility is a direct result of their chemical compositions which contain ions commonly found in the physiological environment such as Ca2+, K+, Mg2+, Na+, and of other ions showing very limited toxicity to body tissues (such as Al3+ and Ti2+). Due to their excellent tribological properties and with their improved fracture toughness and reliability, structural ceramics such as polycrystalline alumina and has been used as hard tissue replacement materials. One remarkable success of bioceramics as implant materials over the last two decades has been the emergence and clinical use of bioactive ceramics that elicit a specific biological response at the interface of the material resulting in the formation of a strong bond between the tissue and the material. These bioceramics include calcium phosphates with hydroxyapatite being the prominent family member, bioglasss, A-W glass–ceramic, and other bioactive glasses and glass–ceramics. However, the brittle nature of ceramics such as alumina and the low strength of bioactive ceramics such as hydroxyapatite have limited their scope of clinical applications. Bioceramics are generally used to repair or replace skeletal hard tissues and their stable attachment to connective tissue varies significantly. Bioceramics can be classified into four groups based on their type of attachment to the surrounding tissues. Dense and nearly inert ceramics attach to the bone by morphological fixation, or growth of bone into surface irregularities.

Hydroxyapatite [$(Ca_{10}(PO_4)_6(OH)_2$], a natural calcium phosphate, forms the mineral component of the skeletal system of vertebrates. Artificial hydroxyapatite is regarded as bioactive since it forms a strong bond with hard tissues, and it has therefore attracted much attention as a substitute material for damaged teeth or bones in dental and orthopaedic applications. The inherent low strength and fracture toughness of hydroxyapatite ceramics prepared ex situ have, however, to

date restricted these ceramics to be used only as implants that are subjected to low stresses, e.g., small unloaded or low loaded implants, coatings on metal implants, and bioactive filler as a powder or a second phase in polymer-based composites. For load-bearing applications, one possibility to overcome this limitation is to use hydroxyapatite as bioactive filler in ceramic and metallic matrix composites. This idea has never been successful, however, because of the deleterious reactions taking place between the hydroxyapatite and the matrix phases [12-14]. Mechanical characterization of spark plasma sintered fully dense quasi-binary system of $Ca_{10}(PO_4)_6(OH)_2$ and tetragonal ZrO_2 has been reported where authors have found that the composite materials are 5 to 7 times stronger and 7 times tougher than monolithic hydroxyapatite ceramics, indicating them to have great potential for a wide variety of clinical applications[15]. In another work it has been reported that the addition of just 3 wt % partially stabilized zirconia increased the fracture toughness of pure HA; that is, the fracture toughness of the HA-zirconia composite was 2 MPa $m^{1/2}$, while the fracture toughness of pure HA was only 1 MPa $m^{1/2}$; the fracture toughness of cortical bone is around 2 MPa $m^{1/2}$. Although pure HA starts to decompose into tricalcium phosphate (TCP) at 1300°C, a second phase forms well below 1300°C in the presence of ZrO_2. [16,17,18,19] Kim et al.[16] enhanced the sinterability of 3 mol % Y_2O_3-ZrO_2 (up to 40 vol %)-HA composites by increasing the green density of composites through cold isostatic pressing and the addition of small amounts of CaF_2.

In the present study, the effect of addition of undoped and doped / stabilized zirconia on the sinterability and mechanical properties of HA compact was investigated. Pure HA, undoped zirconia (ZA), partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystal (TZP) powders were synthesized using wet chemical precipitation route. Both undoped and doped zirconia was added to the extent of 5, 10 and 15 wt% to synthesized HA powder, consolidated into green pellets and pressureless sintered at 1250 C for 4 hours. The sintered pellets were characterized for bulk density measurement, microhardness and bi-axial flexural strength.

CHAPTER # 3

EXPERIMENTAL PROCEDURE

3.1 Preparation of hydroxyapatite powder

- **Precipitation method**:

100 ml aqueous solution of $Ca(NO_3)_2$ was prepared. Then NH_3 solution was added to the solution until pH 10 measured using a pH scale or pH meter. Similarly another 100 ml aqueous solution of $NH_4H_2PO_4$ was prepared. Two solutions were mixed and stirred overnight . Washing and centrifuging were done to get the product and then the product was dried in a drier for 24 hours at 80 °C to get the powder. The dried powder was then calcined at 600 °C for 6 hours.

3.2 preparation of zirconia powder

- **Precipitation method:**

32.5 gm of $ZrOCl_2.8H_2O$ was taken and then NH_3 solution of 20 ml was added to it in 100 ml of water. Then it was stirred magnetically to form a precipitate. Then washing and centrifuging were performed so that all NH_4Cl particles will move out of the solution. The product obtained was dried in a drier for 24 hours at 80°Cand then hard dried mass obtained was ground to get zirconia powder which was calcined.

3.3 Preparation of HA-ZrO_2 composite without any stabilizer

5, 10 and 15 weight % of unstabilised zirconia already calcined at 600°C was taken and mixed with hydroxyapatite separately to make composites of different compositions. Each composition was mixed thoroughly and then pressed at a pressure of 6 tons for 60 seconds to make pellets of 0.5 grams each. This was followed by sintering of the green pellets at a temperature of 1250°C for 4 hours.

3.4 Preparation of TZP powder using CaO as a stabilizer by precipitation method

7.5 mol% $Ca(NO_3)_2$, equivalent to 2.1961 gm, was dissolved in 0.5 mol/L or 0.125 mol/250 ml of $ZrOCl_2$. $8H_2O$ (40.281 gm of $ZrOCl_2$. $8H_2O$ in 250 ml water). Concentrated NH_3 was then added until the pH of the solution is 10 with overnight stirring. Centrifuging, drying and grinding were performed to get powders. Calcination of the as synthesized powders was performed at 600°C for 6 hours.

3.5 Preparation of HA-TZP composite

5, 10 and 15 weight % of calcined TZP powders were taken and mixed with hydroxyapatite already prepared separately to make composites of different compositions. Each composition was mixed thoroughly and then pressed at a pressure of 6 tons for 60 seconds to make pellets of 0.5 grams each. This was followed by sintering of the green pellets at a temperature of 1250°C for 4 hours.

3.6 Preparation of CaO stabilized PSZ using co precipitation method

2.5 mol % CaO (0.737 g of $Ca(NO_3)_2$) was dissolved in 0.5 mol/L of $ZrOCl_2.8H_2O$ was dissolved in 40.281 g of $ZrOCl_2$ in 250 ml water. Concentrated NH_3 was then added until the pH of the solution is 10 or above 10. Then overnight magnetic stirring was done.

3.7 preparation of HA-PSZ composite

5, 10 and 15 weight % of calcined TZP powders were taken and mixed with hydroxyapatite already prepared separately to make composites of different compositions. Each composition was mixed thoroughly and then pressed at a pressure of 6 tons for 60 seconds to make pellets of 0.5 grams each. This was followed by sintering of the green pellets at a temperature of 1250°C for 4 hours.

Table 1: Composition of different batches used for the fabrication of HA pellets

1st batch	2nd batch	3rd batch
HA-5ZrO_2	HA-5TZP	HA-5PSZ
HA-10ZrO_2	HA-10TZP	HA-10PSZ
HA-15ZrO_2	HA-15TZP	HA-15PSZ

3.8 Characterizations:

3.8.1 X-Ray Diffraction (XRD):

The XRD of Hydroxyapatite and zirconia powder synthesized were done using Philips X-Ray diffractometer (PW 1730, Holland) with nickel filtered Cu K_α radiation (λ = 1.5406 A°) at 40 kV and 30mA having a scan range(°2 θ) of 20-80° for both HA and ZrO_2 powders and all the composites prepared.

3.8.2 Bulk Density (BD):

The sintered pellets of the composite were immersed in water which was boiled for 3 hours until no vapours are seen coming out of the pellets. Now the dry, soaked and suspended weight of the pellets is calculated. Bulk Density is calculated by the formula:

$$\text{Bulk Density} = \frac{Dry\ Weight}{Soaked\ Weight - Suspended\ Weight}\ x\ Density\ of\ the\ liquid$$

3.8.3 Vickers Hardness (HV):

The sintered pellets of the composites were polished properly with Emery paper. Now the hardness of the pellets was measured by Vickers Hardness Tester.

Here an indent was given on the pellet and the lens of the instrument was focussed on the diameter of the indent. Vickers hardness is given by the formula:

$H_V = 1.854 * F/d^2$, where F is the indent given, measured in (KgF) and d is mean diameter of the indent measured in (mm)

3.8.4 Bi-axial Flexural Strength:

The diameter and thickness of the pellets were measured. Now the Bi-axial flexural strength of the pellets were measured by UTM machine. Here the pellets are kept on their width and a constant extension per time was fed in the instrument. The instrument measures the maximum load at fracture. Flexural strength is given by formula:

$$\text{Flexural Strength} = \frac{2F}{\pi dt}$$

where F is the maximum load at fracture, d is diameter of the pellet and t is the thickness of the pellet

CHAPTER # 4

RESULTS

AND DISCUSSION

4.1 Results

4.1.1 Phase identification in synthesized powders and sintered compacts

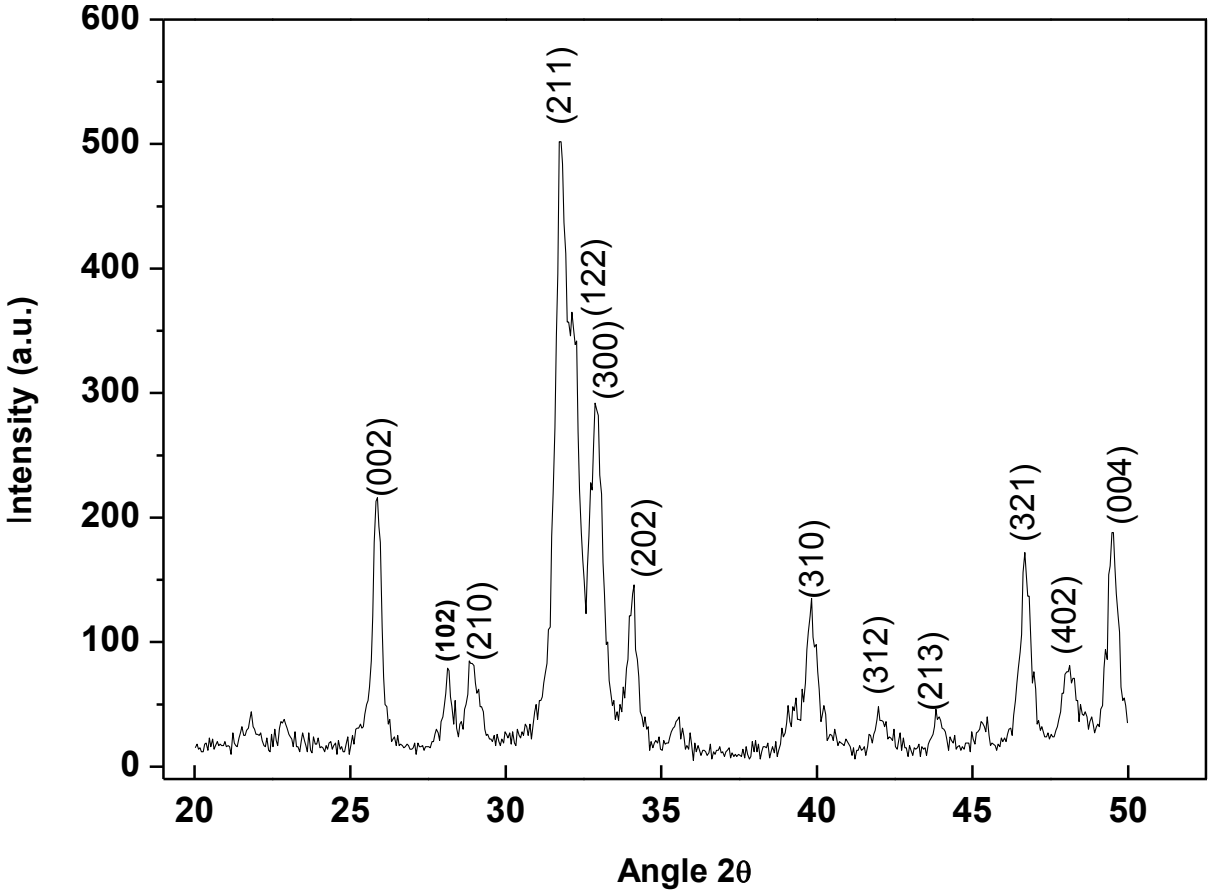


Fig 1: XRD of HA powder calcined at 600 ^{o}C

Figure 1 shows the XRD pattern of synthesized HA powders calcined at 600°C. Phase pure hydroxyapatite powder was obtained using the alkali precipitation method as evident from figure 1.

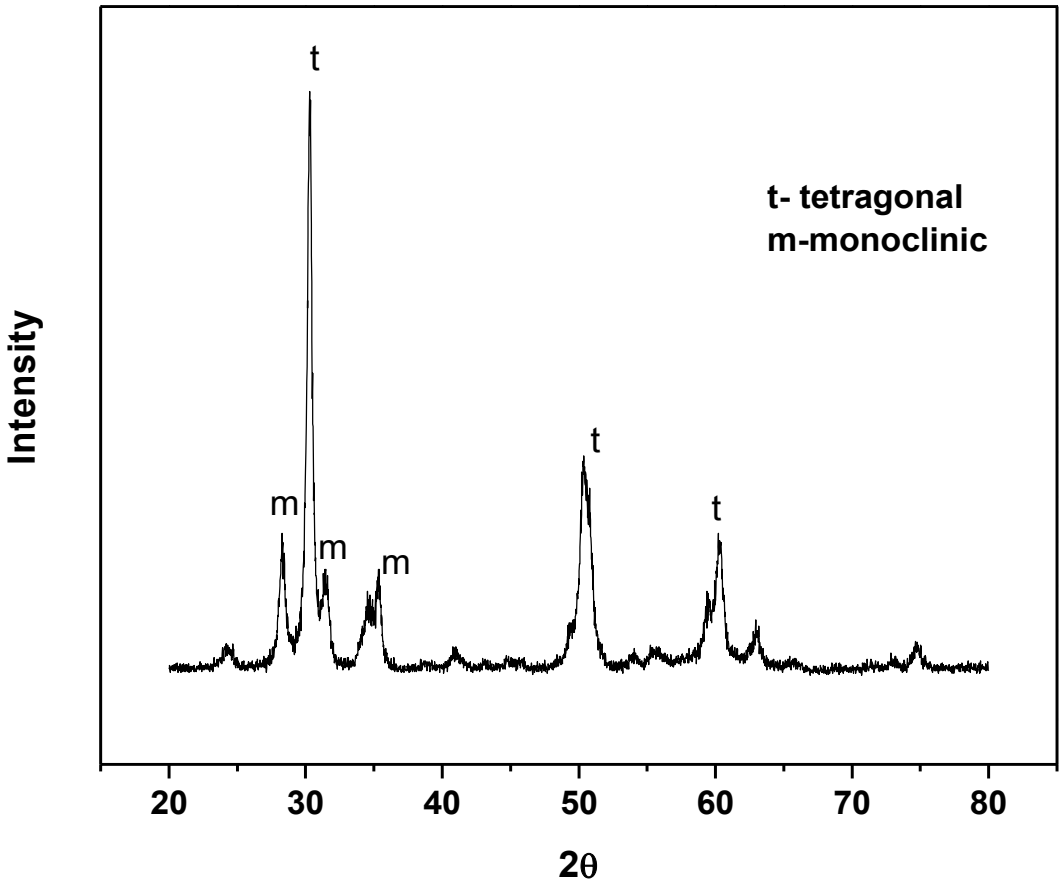


Fig 2: XRD of zirconia powder synthesized using precipitation method without using any stabilizers.

XRD pattern of undoped zirconia powder is shown in figure 2. A mixture of tetragonal and monoclinic phases were observed in the synthesized undopoed ZrO_2 powder after heat treatment at 600^oC.

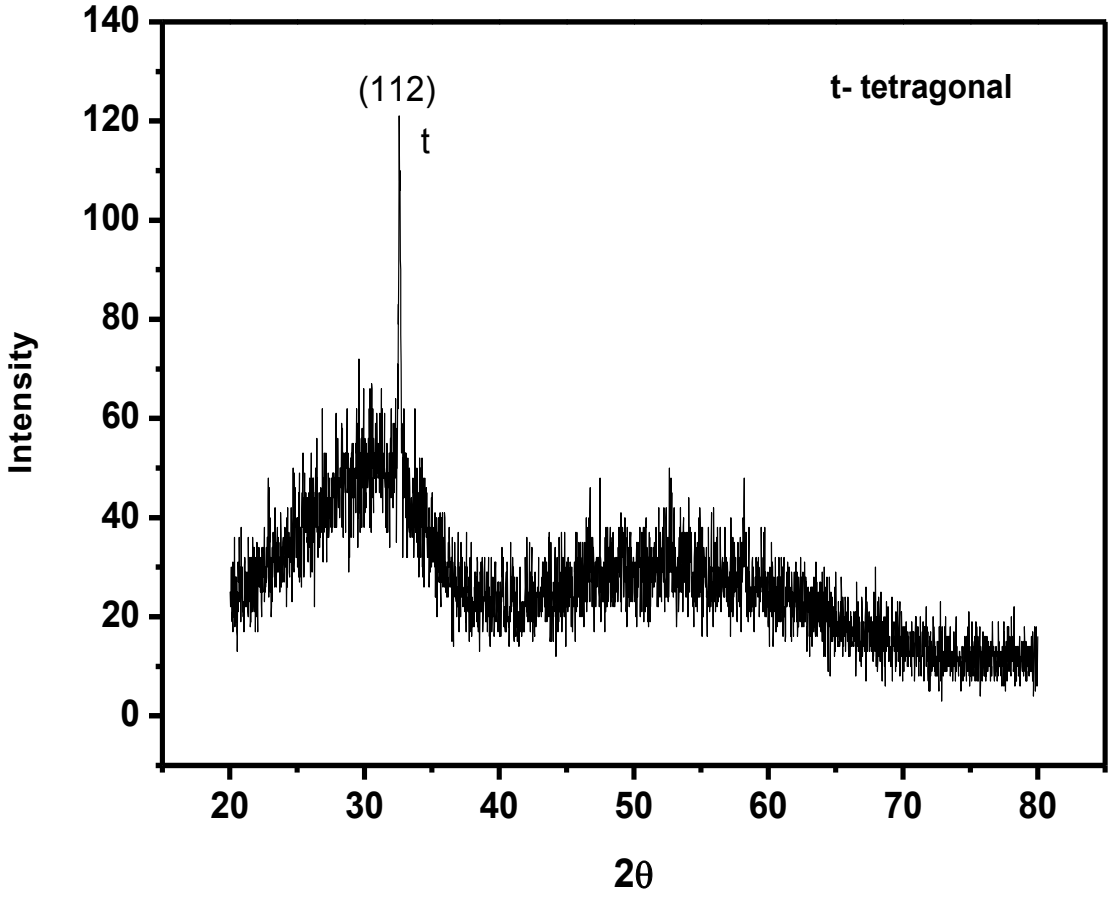


Fig 3: XRD of calcined PSZ powder prepared using 2.5 mol% CaO

XRD pattern of 2.5 mol% CaO doped ZrO_2 powder is shown in fig 3. After heating the powder at 600°C mostly amorphous phases were observed apart from a intense peak at around 32°C which exhibits the presence of tetragonal phase in the powder. From the XRD pattern it is evident that higher temperature of heating or compositional readjustment of the precursor materials is required for the desirable evolution in the synthesized PSZ powder.

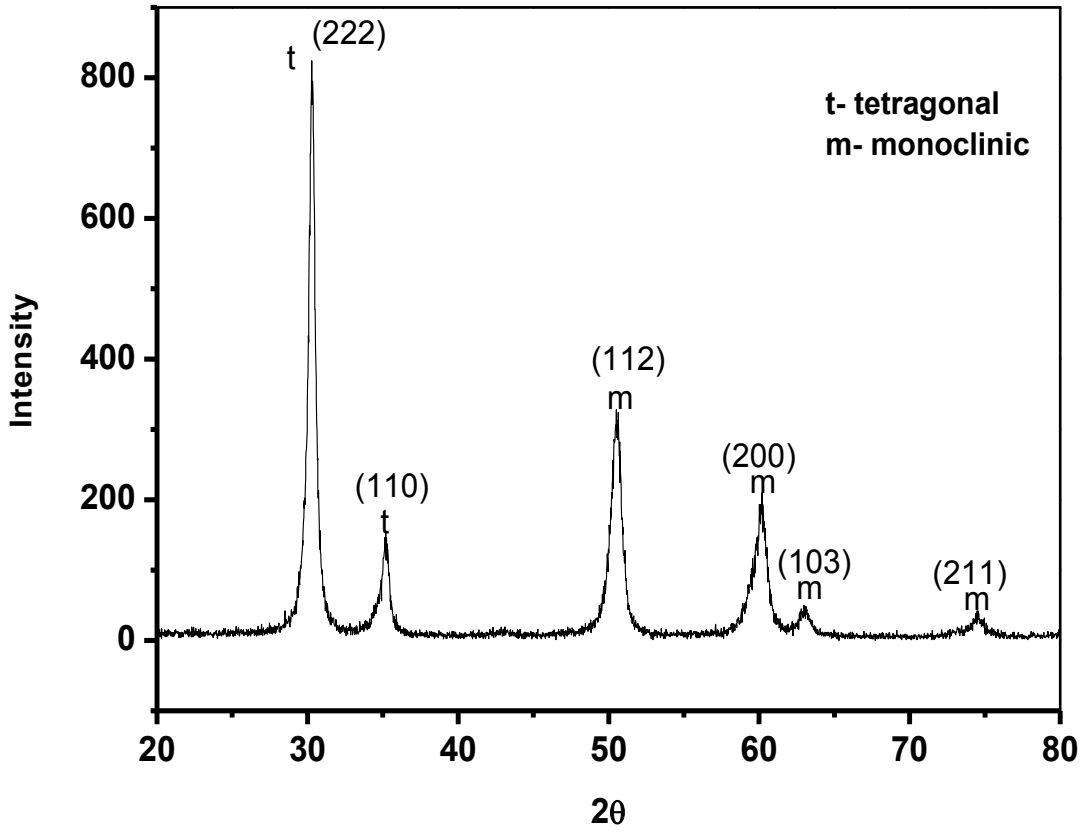


Fig 4: XRD of calcined TZP powder prepared using7.5 mol % CaO as a stabilizer.

Figure 4 shows the XRD pattern of 7.5 mol % CaO doped ZrO_2 powder calcined at 600^oC. Mostly tetragonal phase and some amount of monoclinic phases were observed in the calcined TZP powder. To obtain 100 % tetragonal phase in the desirable TZP powder more amount of dopant addition is required.

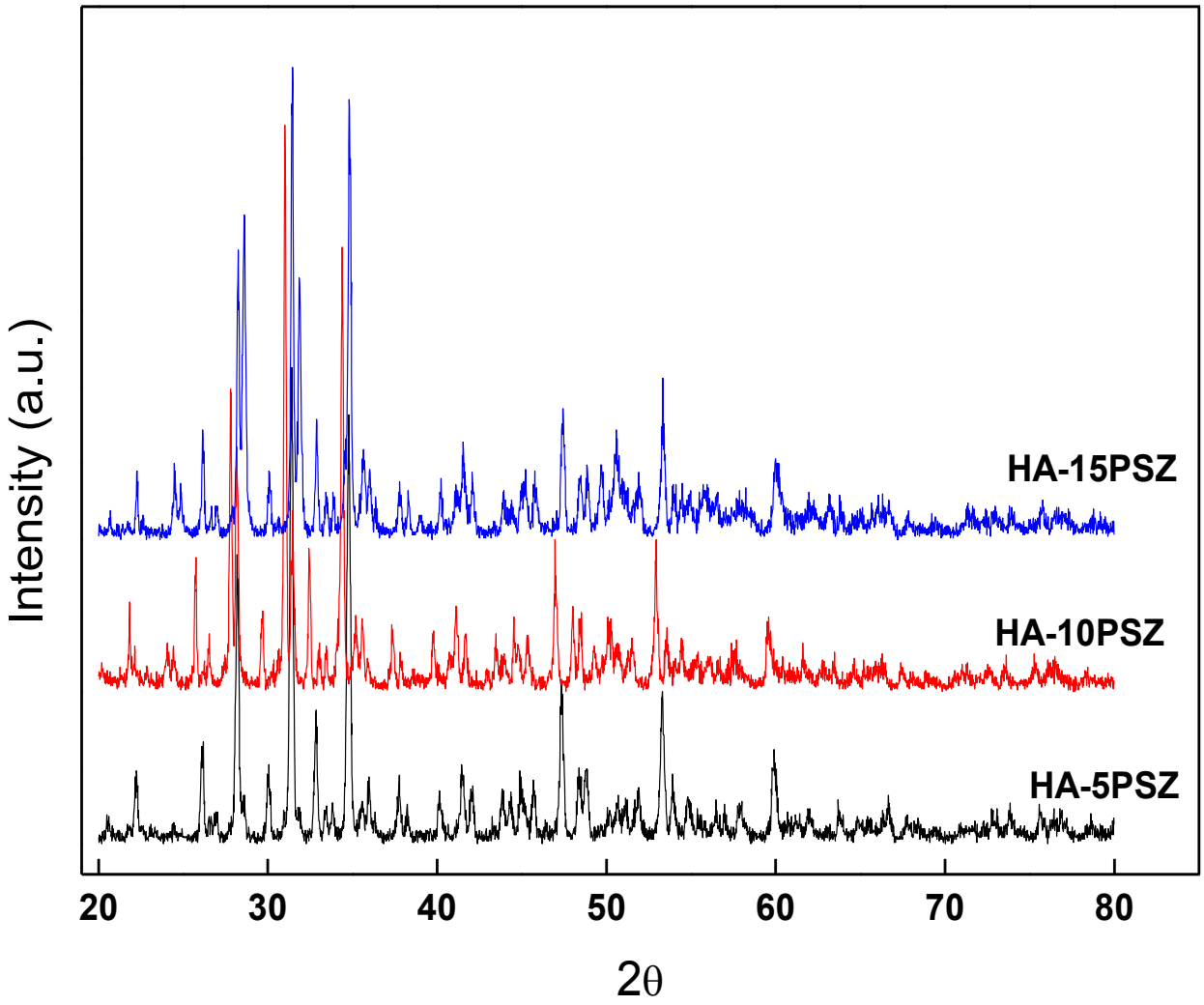


Fig 5: XRD of HA-PSZ compacts sintered at 1250 C

XRD study of HA-PSZ composite sintered at1250 ^{o}C is shown in figure 5. The sintered samples showed the mixture of HA, TCP, $CaZrO_3$ and tetragonal, monoclinic and cubic phases of ZrO_2. In all the compositions of the sintered samples the phases are found to be the same which shows that addition of PSZ upto 15 wt% did not alter the overall phase composition in the sintered samples..

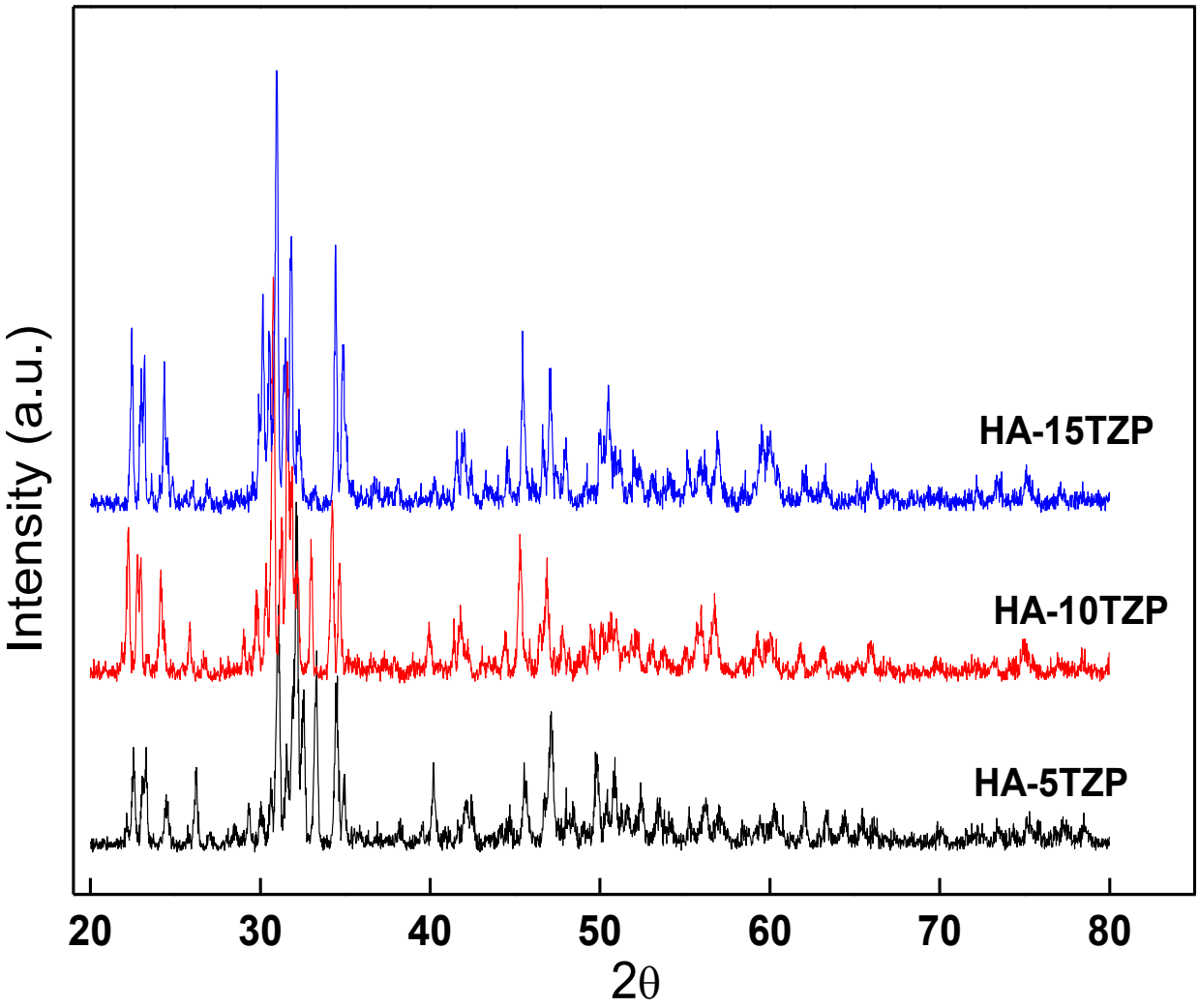


Fig 6: XRD of sintered HA-TZP compacts fired at 1250 °C

The crystalline phases present in the HA-TZP compact sintered at1250^{o}C with different amount of TZP addition is shown in figure 6. Here also a mixture of HA, TCP, $CaZrO_3$ and tetragonal, monoclinic and cubic phases of ZrO_2 were observed after sintering at 1250^{o}C. Thus addition of TZP upto 15 wt% did not alter the overall phase composition in the sintered HA-TZP sample.

4.2 Bulk density analysis of sintered composites

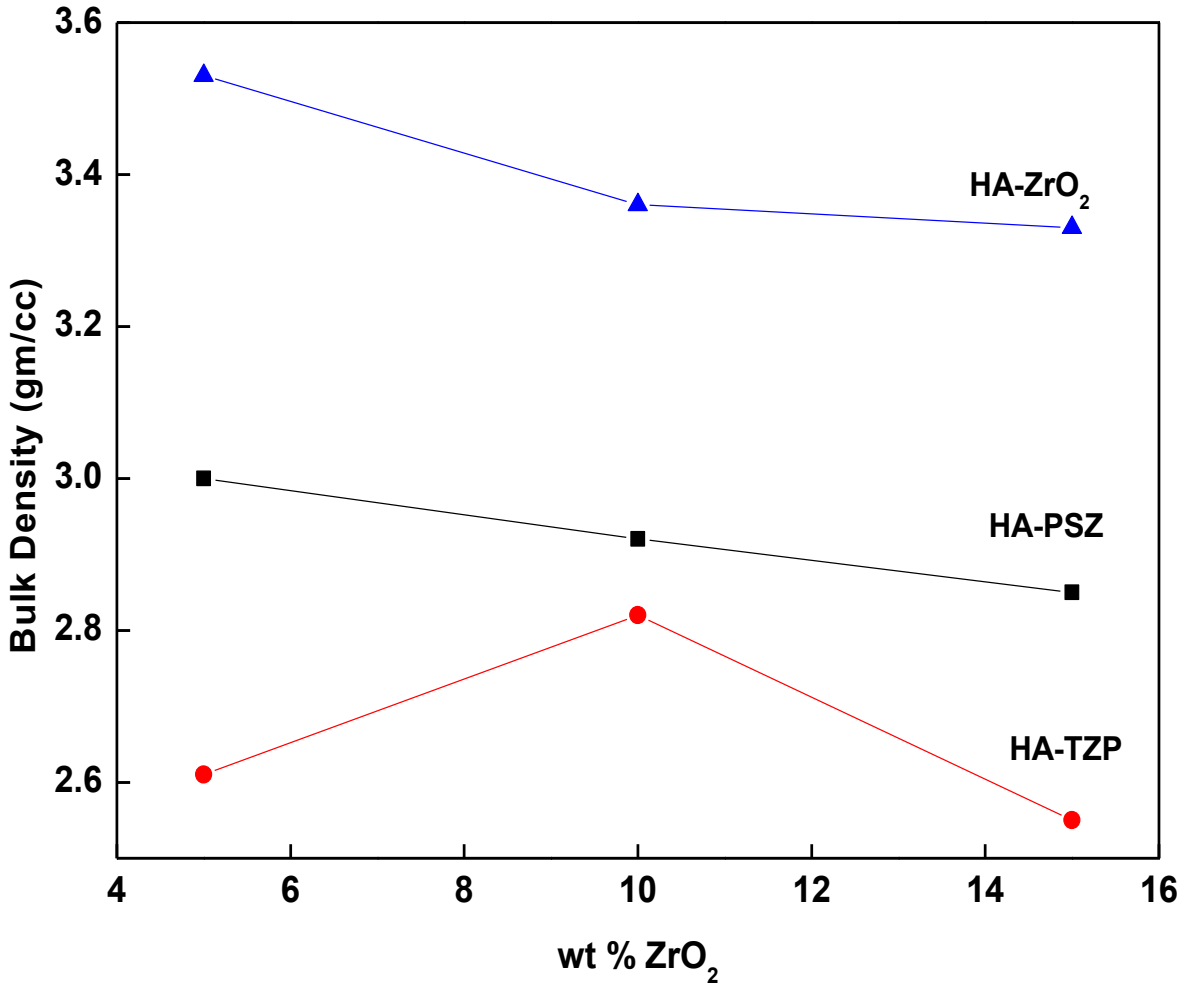


Fig 7: Average values of bulk densities of different sintered composites sintered at 1250 °C

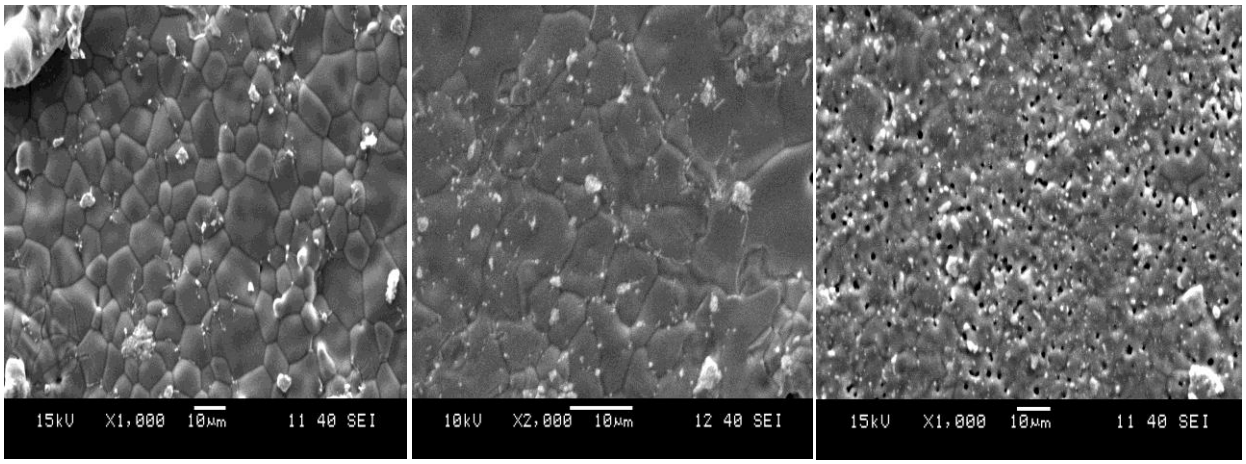
The bulk density values of different composites sintered at 1250°C is shown in table 2 and figure 7. A general trend of decrease in average bulk density (BD) values was observed with increase in zirconia content in the sintered composite except an abnormal increase in BD HA-10TZP composite as compared to other composition. HA-5ZrO_2 composite showed the highest BD value of 3.53 g/cc whereas the BD value for HA-15TZP showed the lowest value of 2.55 g/cc. HA-ZrO_2 composites shows the higher values of BD as compared to the HA-PSZ and HA-TZP composites in all compositions. All the results show that a control over processing parameters as well as amount of

dopants are required to enhance densification kinetics and as a whole bulk density values of the sintered composites.

Table 2: Bulk density values for different composites

Composition	**Bulk density (gm/cc)**
HA-5ZrO_2	3.53
HA-10ZrO_2	3.36
HA-15ZrO_2	3.33
HA-5TZP	2.61
HA-10TZP	2.82
HA-15TZP	2.55
HA-5PSZ	3
HA-10PSZ	2.92
HA-15PSZ	2.85

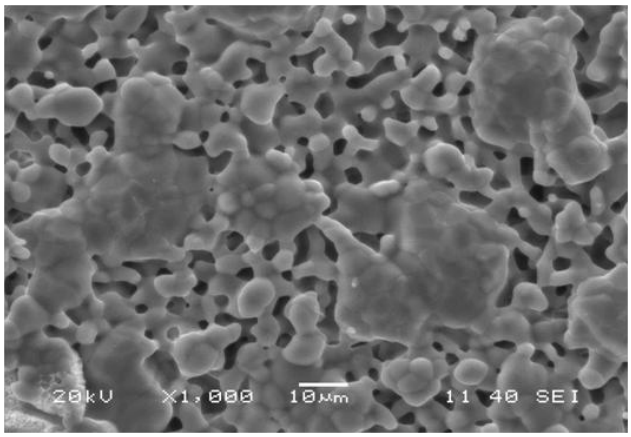
4.3: Microstructural analysis of sintered composite



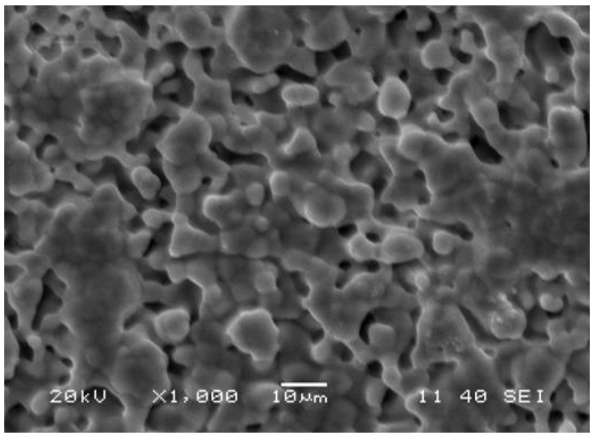
HA- 5ZA **HA-10ZA** **HA-15ZA**

Fig 8: SEM of HA- undoped ZrO_2 composite with varying composition sintered at 1250 ^oC

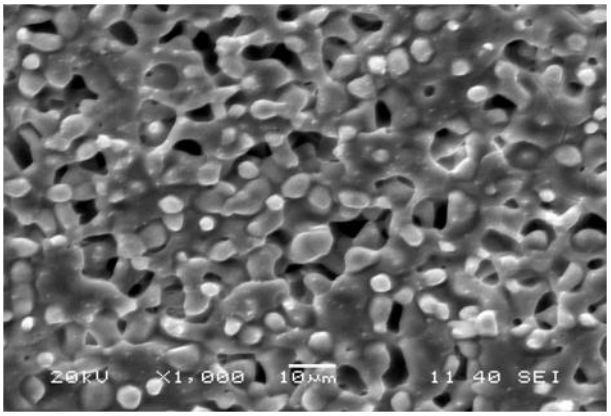
SEM micrographs of HA undoped ZrO_2 composite sintered at 1250^oC are shown in figure 8. Porous microstructures were observed in HA-15TZP sample. From the micrographs it is evident that addition of increasing amount of ZrO_2 led to increase in porosity in the sintered samples. Also addition of ZrO_2 influenced the grain size of the sintered sample as revealed from the fact that HA-5ZrO_2 showed finer grain structure as compared to HA-10ZrO_2 sample.



5% PSZ



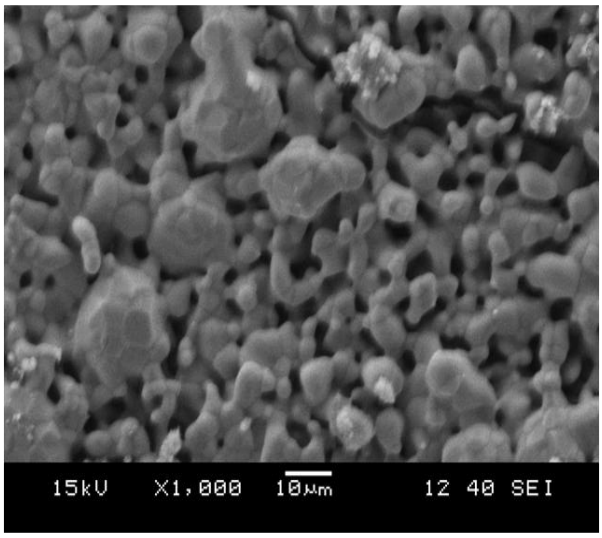
10% PSZ



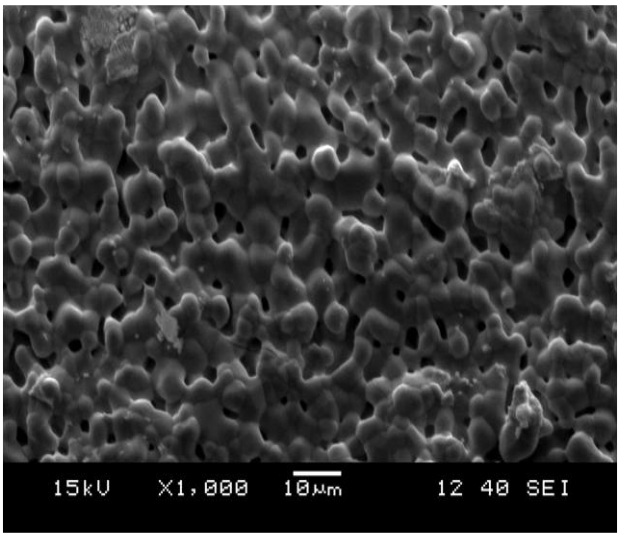
15%PSZ

Fig 9: SEM of HA- PSZ composite with varying composition sintered at 1250 ^{o}C

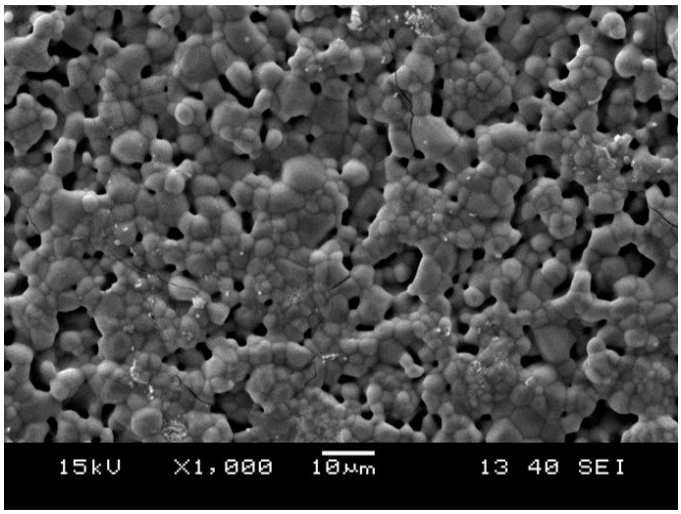
The microstructures of HA-PSZ composites with varying composition sintered at1250^{o}C are shown in SEM micrographs of figure 9. All the samples showed porous microstructure which is consistent with lower BD values in all the composites.



HA-5% TZP



HA-10% TZP



HA-15% TZP

Fig 10: SEM of HA- TZP composite with varying composition sintered at 1250°C

Microstructures of HA-TZP composites with varying composition sintered 1250°C are presented in the SEM micrographs in fig 10. As expected from the lower BD values in HA-TZP samples, a porous microstructures in all the HA-TZP composites were observed. As reflected in higher BD values of HA-10TZP samples, slightly lower degree of porosity was observed in the sintered microstructure of HA-10TZP sample.

4.4 Mechanical Characterization of HA- zirconia composite

4.4.1 Variation in hardness with change in composition in sintered composite

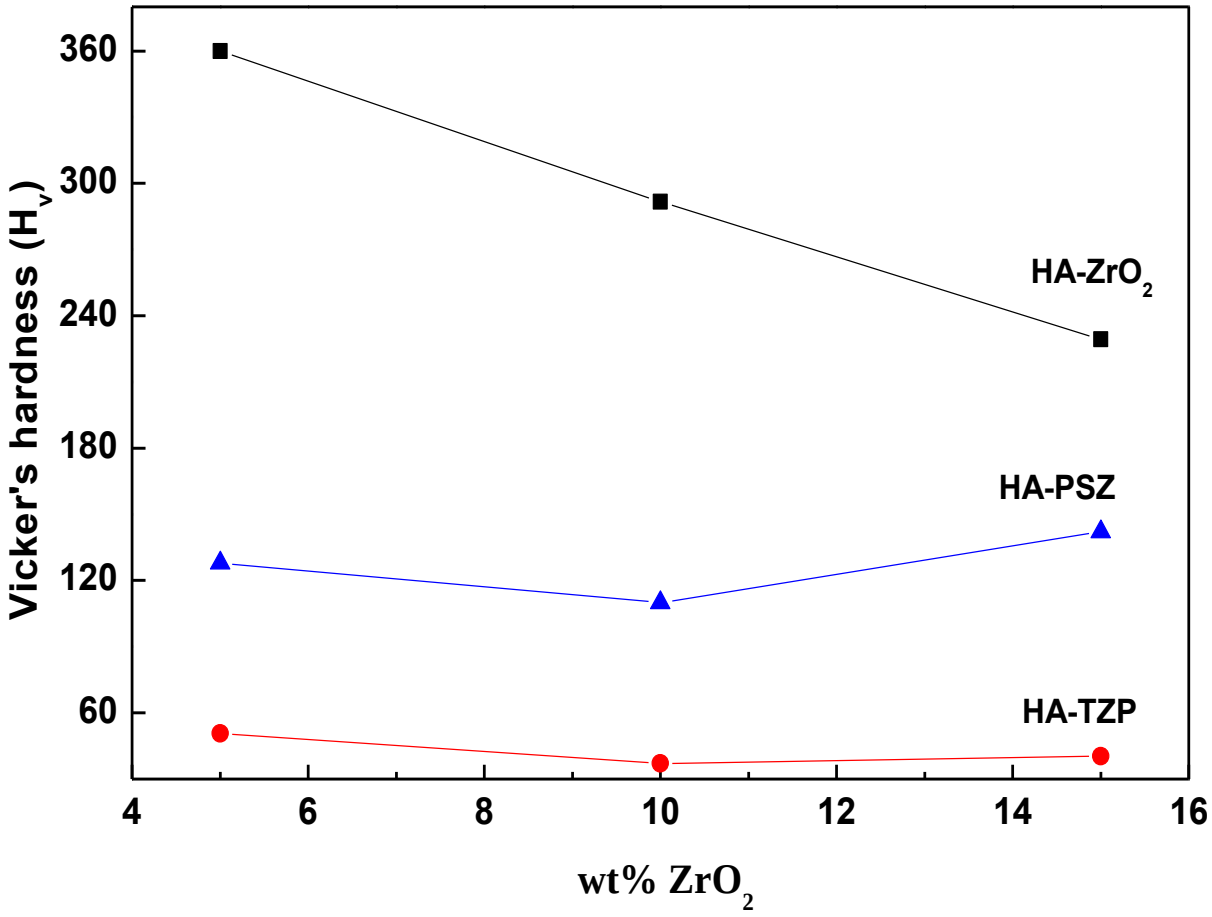


Fig 11: Comparison of Vicker's hardness of the sintered composites fired at 1250 ^{o}C

A comparison of Vicker's hardness values in different sintered composites is shown in figure 11. As expected HA-ZrO_2 composite showed the higher hardness values as compared to the HA-PSZ and HA-TZP because of its higher bulk density and lower porosity. In HA-ZrO_2 composite the hardness value decreased with increase in ZrO_2 content in the composite. The 5 wt% HA-ZrO_2 composite showed the highest hardness value of 360 H_V (3.53 GPa) whereas the lowest value of hardness of 37 H_V was observed in HA-10TZP. HA-PSZ samples showed higher hardness values as compared to HA-TZP samples in the compositions.

Table 3: Average hardness values of different composites

composition	Vicker's hardness (H_V)	Vicker's hardness (GPa)
HA-5ZrO_2	360	3.53052
HA-10ZrO_2	291.7	2.860702
HA-15ZrO_2	229.3	2.248745
HA-5TZP	50.7	0.497215
HA-10TZP	37	0.362859
HA-15TZP	40.4	0.396203
HA-5PSZ	128	1.255296
HA-10PSZ	110	1.07877
HA-15PSZ	142	1.392594

4.4.2 Variation in bi-axial flexural strength with change in composition of sintered composite

The variation in Bi-axial flexural strength with change in compositions in the sintered HA-ZA, HA-PSZ and HA-TZP composites is shown in figure 12. As expected HA-ZA showed higher bi-axial flexural strength as compared to HA-PSZ and HA-TZP composites. HA-10ZA showed the highest value of flexural strength of 2.61 MPa whereas HA-5TZP showed the lowest flexural strength. The remarkably higher value of flexural strength in HA-ZA sample as compared to HA-PSZ and HA-TZP is consistent with the fact that the strength decreases exponentially with increase in porosity in the sintered microstructures.

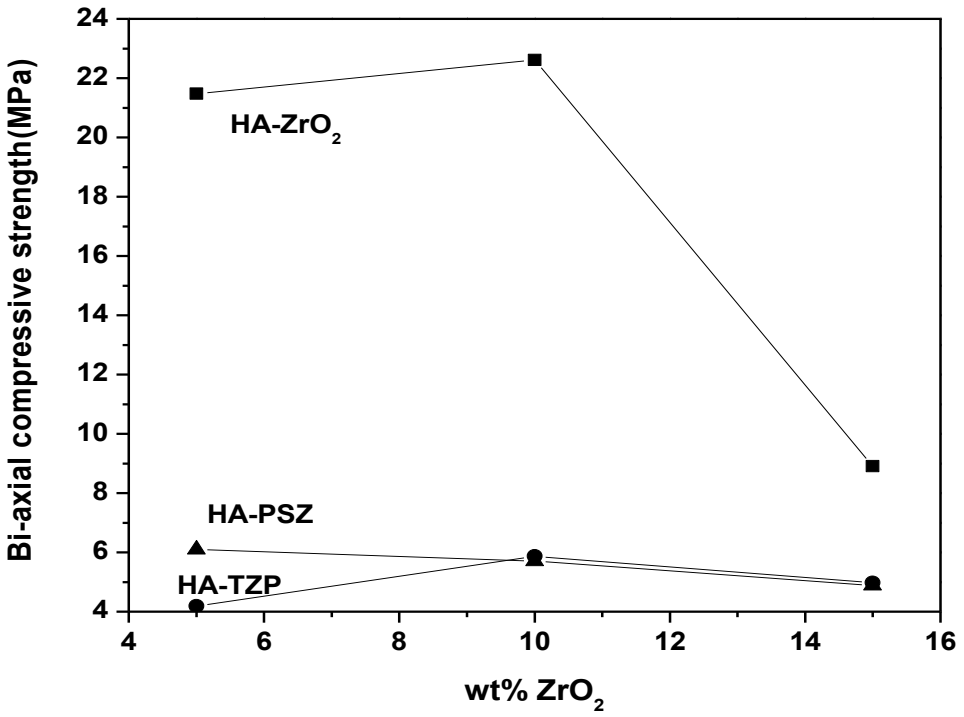


Fig 12: Comparison of bi-axial flexural strength of all sintered compacts sintered at 1250 ^{o}C

Table 4: Bi-axial flexural strength values of different composites

Composition	Bi-axial flexural strength (MPa)
HA-5ZrO_2	21.48
HA-10ZrO_2	22.61
HA-15ZrO_2	8.91
HA-5TZP	4.19
HA-10TZP	5.87
HA-15TZP	4.97
HA-5PSZ	6.10
HA-10PSZ	5.70
HA-15PSZ	4.89

Fig 13(a-i) show the load v/s elongation behaviors of all the sintered composites which were used for the calculation of bi-axial flexural strength.

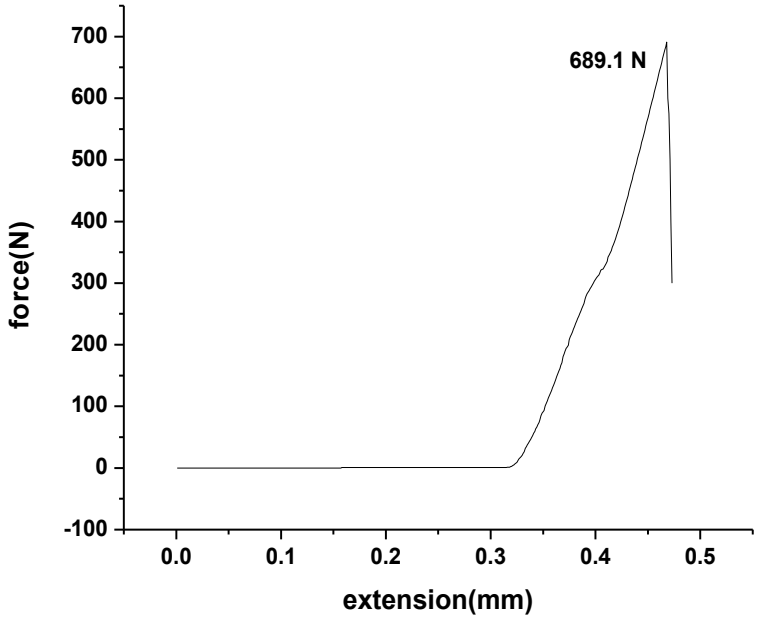


Fig13a: Force v/s extension curve of HA-5ZrO_2 with the corresponding breaking force

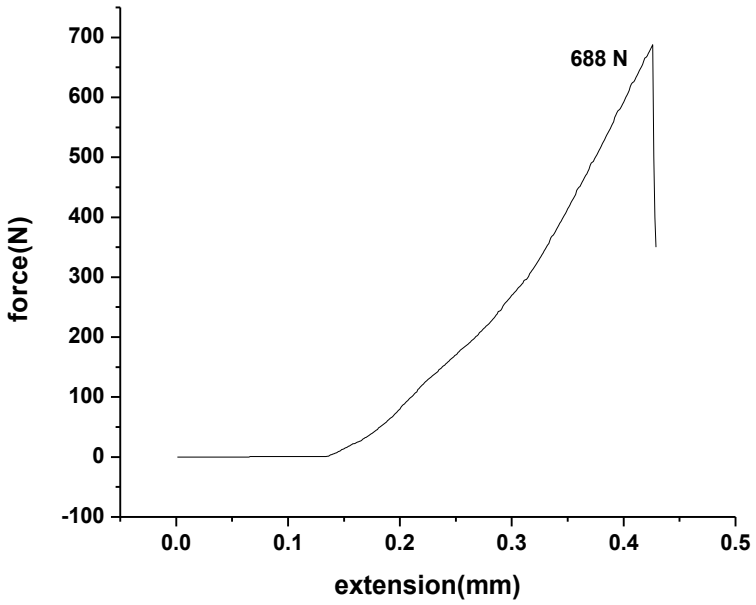


Fig13b: Force v/s extension curve of HA-10ZrO_2 with the corresponding breaking force

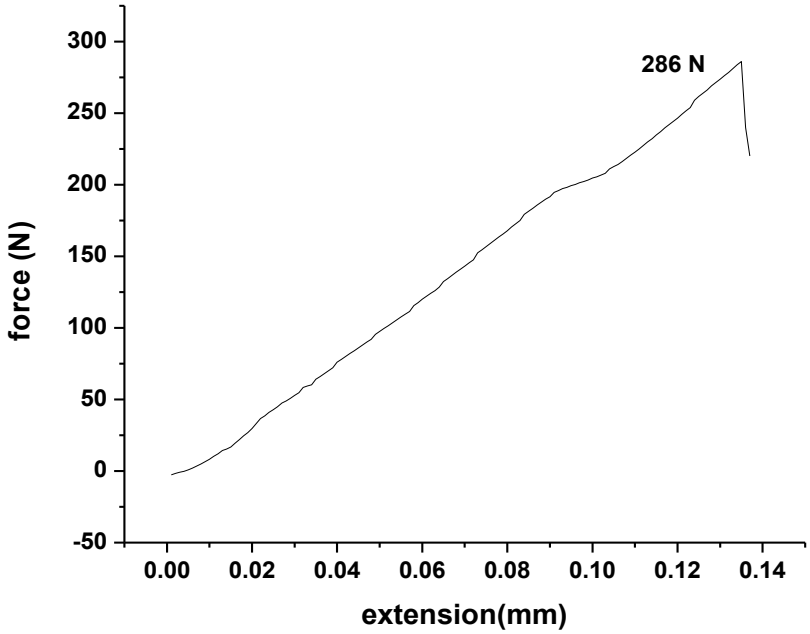


Fig13c: force v/s extension curve of HA-15ZrO_2 with the corresponding breaking force

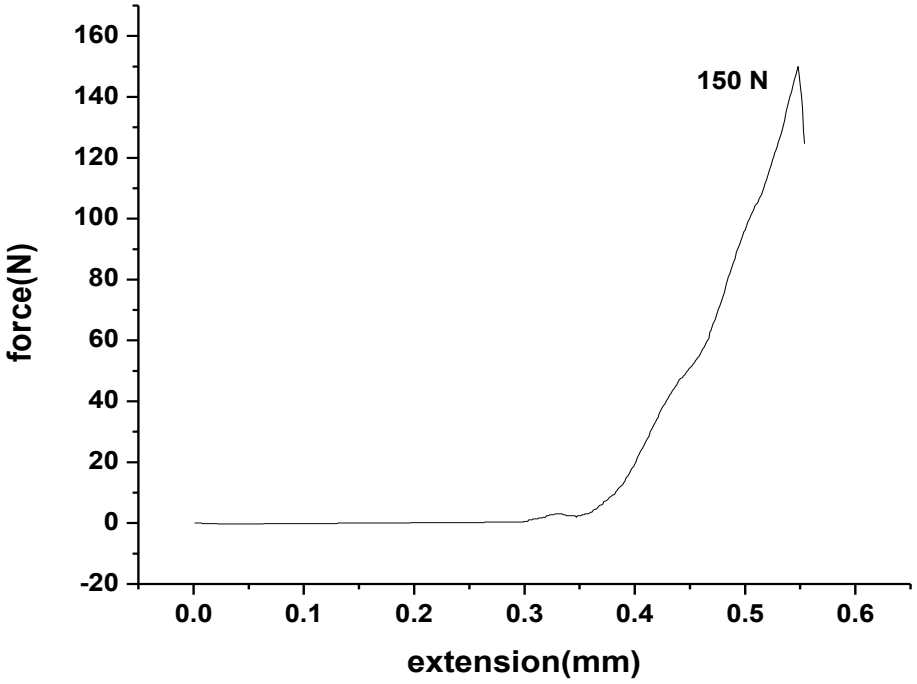


Fig13d: Force v/s extension curve of HA-5TZP with the corresponding breaking force

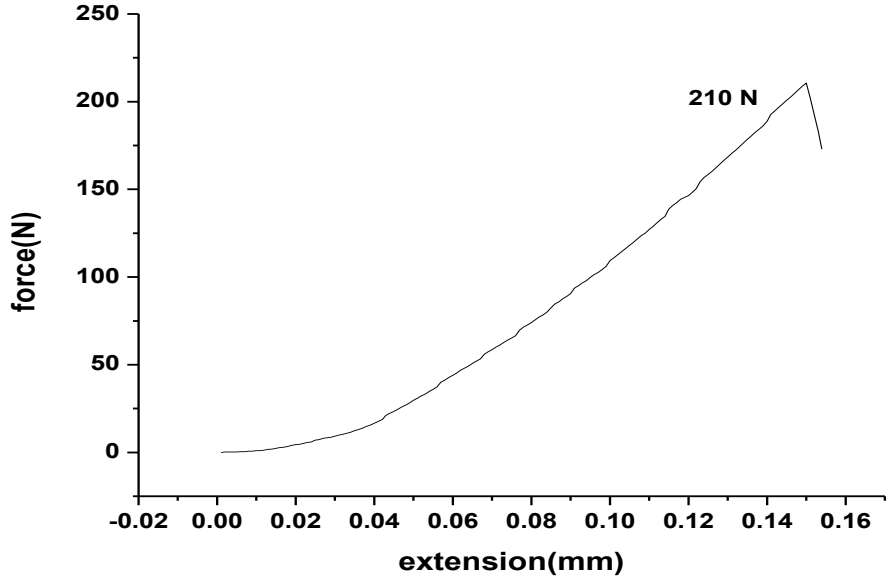


Fig13e: force v/s extension curve of HA-10TZP with the corresponding breaking force

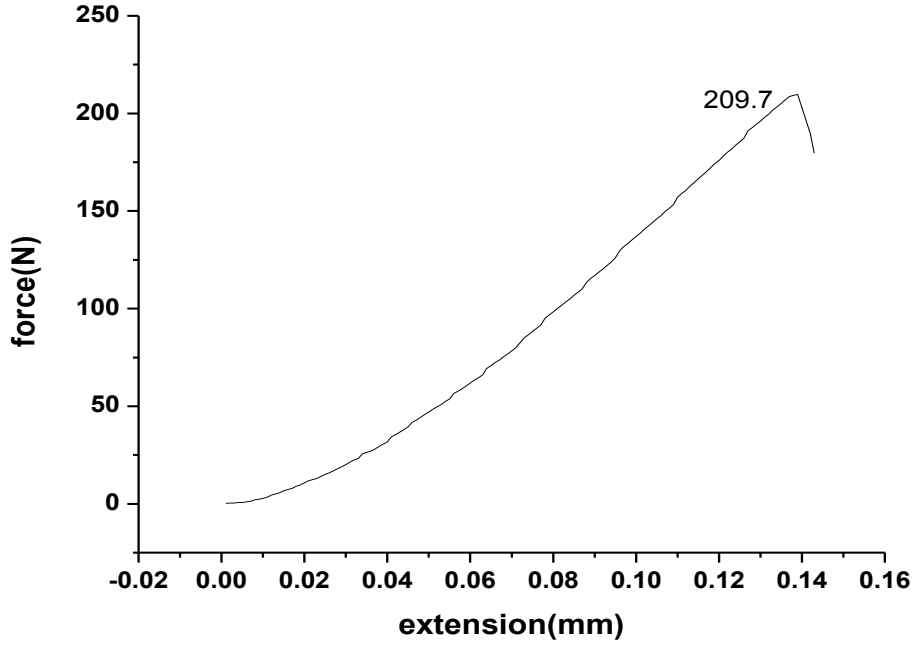


Fig13f: Force v/s extension curve of HA-15TZP with the corresponding breaking force

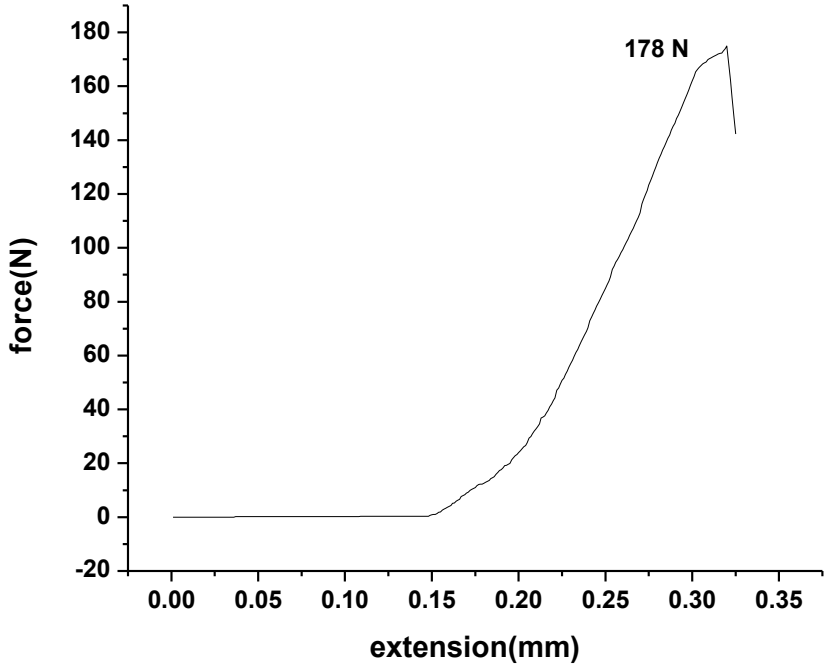


Fig13g: **Force v/s extension curve of HA-5PSZ with the corresponding breaking force**

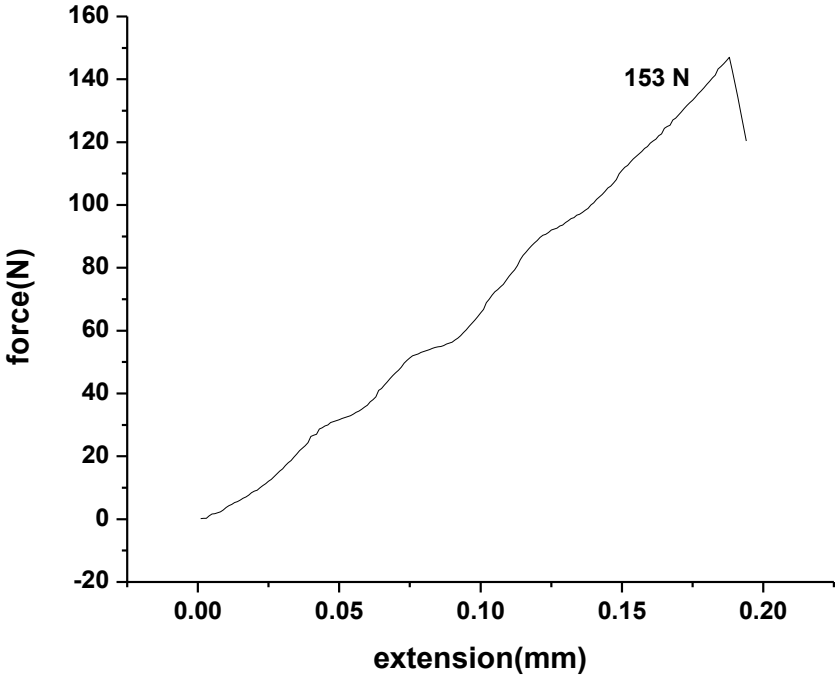


Fig13h: **force v/s extension curve of HA-10PSZ with the corresponding breaking force**

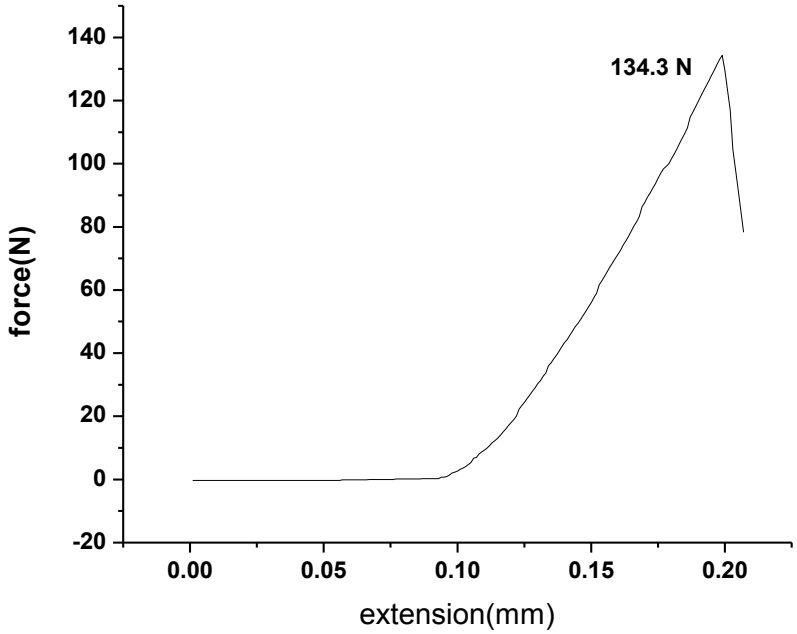


Fig13i: force v/s extension curve of HA-15PSZ with the corresponding breaking force

4.2 Discussion

HA powder was synthesized by the alkali precipitation route as per the following equation (1). Only HA phase was precipitated that is why a phase pure HA powder was obtained.

$10\ Ca(NO_3)_2.4H_2O + 6NH_4H_2PO_4 + 14NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18NH_4NO_3 + 16H_2O$....(1)

ZrO_2 was synthesized from $ZrOCl_2.8H_2O$. First NH_4OH reacts with $ZrOCl_2.8H_2O$ to form $Zr(OH)_4$ as per equation (2). The obtained $Zr(OH)_4$ was heated at 600°C to get ZrO_2 powder after dehydroxylation as per equation (3).

$ZrOCl_2 + NH_4OH \rightarrow Zr(OH)_4 + 2NH_4Cl$.....(2)

$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O$.....(3)

Ca^{2+} was used as dopant to stabilize metastable phases of ZrO_2 at room temperature. Ca^{2+} was incorporated into the lattice structure of ZrO_2 and resulted in disorder of the ZrO_2 which in turn stabilized the metastable phases such as tetragonal phase. In the sintered sample tricalcium phosphate (TCP) was observed because of degradation of HA in presence of ZrO_2 and with increasing amount of ZrO_2 a gradual increase in amount of TCP phase was observed in the sintered pellets. CaO release by the HA during sintering at 1250 C led to the formation of Ca stabilized cubic zirconia and/or $CaZrO_3$ with accelerated degradation of HA. With increase in ZrO_2 addition densification of HA-ZA composites hampered because of effective pinning of ZrO_2 at HA grain boundary (GB) restricting GB diffusion. The fact was reflected in the lower bulk density values of the composite with increase in ZrO_2 content. Both PSZ and TZP added HA composite showed lower bulk density compared to HA-ZA composite because of enhanced phase transformation in the PSZ and TZP phases during sintering. As expected with decrease in bulk density and with increase in porosity both hardness and flexural strength of the composite decreased. That is why HA-5ZA composite having the highest bulk density showed the highest hardness and bi-axial flexural strength among all the samples.

5. Conclusions:

In summary, this study was aimed at improving mechanical strength of HA based ceramics by adding both stabilized and undoped zirconia. With increase in zirconia content from 5 wt% to 15 wt% in HA matrix the bulk density was decreased and the highest bulk density and lowest porosity were obtained in 5 wt% ZrO_2 doped samplesafter sintering the composites at 1250 C for 4 hours. Increased ZrO_2 loading effectively pins grain boundaries preventing complete densification. In general, addition of undoped zirconia to HA matrix found to increase the sintered density of the resulting composite as compared to PSZ and TZP doped composites. 5 wt % undoped ZrO_2-HA composite showed the highest hardness and bi-axial flexural strength among all the sintered composites because of higher bulk density and lower porosity in the sintered microstructure. Increased ZrO_2 loadings retard mechanical strength due to the increased formation of TCP and increasing porosity. The mechanical properties of this category of composite materials can be further optimized by carefully tailoring the microstructure. Thus, increasing the grain size of the formed tetragonal zirconia phase may enhance the fracture toughness; using more fine hydroxyapatite powders may retain the flexural strength at an even higher lever; and introducing micro-pores into the structure may reduce the Young's modulus. Further, the effect of zirconia addition on overall bioactivity of these types of HA base composites requires in details biological characterization of sintered composites using osteo-precurssor or osteoblast cell lines. Thus a delicate balance must be reached between increasing mechanical properties of HA without decreasing osteoblast cytocompatibility properties through zirconia addition. The present work thus opens up possibilities of producing bioactive hydroxyapatite-containing ceramic composites with a variety of mechanical properties that can meet the requirement of various biological load-bearing applications.

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